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(54)【発明の名称】　結晶性の測定方法

【特許請求の範囲】

【請求項１】紫外分光法を用いて結晶の結晶性を測定する方法であって、

被測定体の表面反射スペクトル曲線における結晶のグレインサイズに依存する２つの極小点または変曲点を求め、

当該点を結ぶ線、または当該点近傍の点を結ぶ線と上記スペクトル曲線との囲む面積から、当該結晶のグレインサイズを測定する

結晶性の測定方法。

【請求項２】紫外分光法を用いて結晶の結晶性を測定する方法であって、

被測定体の表面反射スペクトル曲線における結晶のグレインサイズに依存する２つの極小点または変曲点を求め、

当該点間の上記スペクトル曲線の最大点から上記当該点を結ぶ線、または当該点近傍の点を結ぶ線へおろした垂線の高さから、当該結晶のグレインサイズを測定する

結晶性の測定方法。

【発明の詳細な説明】

〔産業上の利用分野〕

本発明はＳｉ，Ｇｅ，Ｃ，ＳｉＣ，ＧａＡｓ等の共有結合半導体結晶の結晶性の測定方法に関する。本発明は、例えばＳｉ結晶を扱う産業分野、例えば半導体分野において、ＰｏｌｙＳｉ（多結晶シリコン）の結晶性や、Ｓｉ基板表面の結晶性を測定するためなどに利用することができる。

〔発明の概要〕

本発明は、被測定体の表面反射スペクトル曲線における結晶のグレインサイズに依存する２つの極小点または変

曲点を求め、当該点を結ぶ線、または当該点近傍の点を結ぶ線と上記スペクトル曲線との囲む面積、あるいは、当該点間の上記スペクトル曲線の最大点から当該点を結ぶ線、または当該点近傍の点を結ぶ線へおろした垂線の高さから、当該結晶のグレインサイズを測定することにより、従来は長時間を要し、かつプロセス内での測定が困難であった結晶性の測定を、簡便にしかも半導体プロセスなどにおけるインライン測定をも可能にした、結晶性の測定方法に関する。

〔従来の技術〕

従来、各種分野で用いられる結晶Ｓｉについて、その結晶性特にその結晶グレインサイズを簡便迅速に測定することは困難であった。特に、結晶Ｓｉを材料とする製造工程において、該工程中に結晶のグレインサイズを測定することは行われていない。

例えばＰｏｌｙＳｉは、各種電子デバイスにおいて多方面に利用されているが、これまではＰｏｌｙＳｉの自動製造工程中においてモニター可能であったのは、膜厚、屈折率、ダスト程度であり、そのグレインサイズはＰｏｌｙＳｉの種々の特性上重要であり、特にＰｏｌｙＳｉを抵抗体や薄膜トランジスタとして用いる時の重要なファクターであるにも拘らず、インプロセスモニターの対象とされることがなかった。これは、従来ＰｏｌｙＳｉのグレインサイズの測定がＴＥＭを用いて行われていたためである。即ち、ＴＥＭによる測定においては透過電子顕微鏡を用いて一つ一つのグレインのサイズを測定する必要があるため、サンプルを薄膜化する等の測定試料作製に長時間を要し、しかもコストが高くなるからである。また、Ｓｉ基板表面の結晶性も同様にその特性上重要なファクターであり、ＲＢＳ方法による測定は可能であるが、ＲＢＳ方法は測定時間が長くなる上に表層の極く薄い範囲（例えば100Å以下の範囲）内の測定が困難であるという欠点を有している。

〔発明が解決しようとする問題点〕

上述したように、従来の測定方法は、いずれも煩雑で長時間を要し、従って例えば半導体製造プロセスインラインにおけるグラインサイズのモニターに適用することができないという問題がある。

本発明の目的は、この問題を解決して、簡単な操作で、短時間かつ低コストで、しかも非破壊の状態において結晶のグレインサイズを知ることによりその結晶性を簡便に測定でき、かつ各種工程中にインプロセスでこの測定を行うことをも可能にした、結晶性の測定法を提供することにある。

〔問題を解決する技術的手段〕

本発明に係る例えばＳｉ結晶性の測定方法は、紫外分光法を用いてＳｉ結晶の結晶性を測定するものであって、被測定体の表面反射スペクトル曲線におけるＳｉ結晶のグレインサイズに依存する２つの極小点または変曲点を求め、当該点を結ぶ線、または当該点近傍の点を結ぶ線

と上記スペクトル曲線との囲む面積、あるいは、当該点間の上記スペクトル曲線の最大点から当該点を結ぶ線、または当該点近傍の点を結ぶ線へおろした垂線の高さから、当該Ｓｉ結晶のグレインサイズを測定する技術的手段をとることにより、上記従来技術の問題を解決する。

紫外分光法を用いた場合の被測定体の表面反射スペクトル曲線において、Ｓｉ結晶のグレインサイズに対応するのは、通常、235nmと330nmにおけるスペクトル形状である。即ちＳｉ結晶、特にＰｏｌｙＳｉの結晶性を表すのは270～280nmのピークであり、この両側の、235nmと330nm付近において、極小または変曲点が現れる。従って、この２つの極小点または変曲点を結ぶ線と、スペクトル曲線とが囲む面積、あるいは、２つの点間のスペクトル曲線の最大点から、２つの点を結ぶ線へおろした垂線の高さは、上記Ｓｉ結晶の結晶性を表すピークに対応するデータとなる。よってこれを用いてＳｉ結晶のグレインサイズを知ることができ、これによりＳｉ結晶性を測定できる。上記極小点または変曲点を直接結ぶのでなく、例えば当該極小点や変曲点近傍に接するように接線を引いた場合の、該接線と上記スペクトル曲線とが囲む面積、あるいは、２つの点間のスペクトル曲線の最大点から接線へおろした垂線の高さも、グレインサイズを表すものとして利用できる。このように接点を利用できるほか、その他上記極小点や変曲点と関連をもつ点を結んでそれとスペクトル曲線との囲む面積、あるいは、その関連をもつ点間のスペクトル曲線の最大点からそれへおろした垂線の高さを求めて、同様にグレインサイズと関係するデータとするのでもよい（以下このような面積をピーク面積といい、このような垂線の高さをピーク高さという）。

〔発明の作用〕

上記のように、本発明の測定方法によれば、被測定体の表面反射紫外分光スペクトルによりグレインサイズを表すデータが得られる。従って例えばＴＥＭにより予め正確にグレインサイズを測定したものについて、各グレインサイズに固有の表面反射スペクトルを得ておき、各グレインサイズについての上記面積あるいは上記高さのデータを調べておけば、これと上記実測により得たデータとを比較対応させることにより、被測定体の結晶のグレインサイズを知ることができる。

この測定方法によれば必要なデータを得るのに被測定体の表面反射スペクトルを測定するだけでよいので、簡便にしかも短時間で測定ができ、しかも被測定体を非破壊で測定できる。このため、本発明は、インラインでの結晶性測定法としても用いることができ、インプロセスモニターとして適用することもできる。

〔発明の実施例〕

以下、本発明の一実施例について述べる。但し、当然のことではあるが、本発明は以下述べる実施例にのみ限定されるものではない。

この実施例は、本発明を、紫外反射スペクトルを用いてＰｏｌｙＳｉのグレインサイズを測定する方法に適用したものである。具体的には可視光の分光光度計を用いて表面反射スペクトルを測定した。

本実施例の方法によれば、グレインサイズ（Ｒ）と反射ピーク面積（Ａ）との間には次式のような関係がなりたつので、これを用いてグレインサイズを測定できる。この式は、下記に述べる条件でいくつかのサンプルについてＴＥＭによって予め測定されたグレインサイズと、その各グレインサイズについて予め測定された固有の反射ピーク面積に関するデータに基づいて得られるものである。

Ａ＝２７×log（Ｒ）－２０

（但し、Ａは単結晶シリコンを100とした場合のピーク面積）

以下、この式を導き出すに至った実験の経過を示す。

第１図は石英上に堆積して形成したＰｏｌｙＳｉの典型的な反射スペクトル曲線（イ）を示す。このＰｏｌｙＳｉの膜厚は800Å、堆積温度は610℃である。なお反射スペクトル測定の際、走査速度は中速とし、スリットは2.0nmとして測定した（以下同じである）。

第２図は第１図のＰｏｌｙＳｉにSi^+を40keV、１×$10^{15}cm^{-2}$の条件でイオン注入し、600℃で15時間アニールして得たサンプルの場合の反射スペクトルを示すグラフ（ロ）である。この中で270～280nmの範囲に現れるピークがＰｏｌｙＳｉの結晶性を表すピーク波形である。なお、400nm以上のスペクトルはＰｏｌｙＳｉと石英との間の干渉特性を表しているものであり、これは膜厚との関係を表す波形である。第１図と第２図との比較によって明らかなように、Si^+イオン注入、アニールを行った第２図のサンプルの方がピークが高いものとなる。このようにスペクトルがピークであるときの面積を算出し、ＴＥＭによって予め測定したＰｏｌｙＳｉのグレインサイズとの間で相関関係を調べた。

まず、測定用のサンプルとして次の４種類のものを用いた。

ａ．単結晶　Ｓｉ。

ｂ．数千ÅのグレインをもつＰｏｌｙＳｉ。

（Si^+をイオン注入し、600℃で15時間アニールしたＰｏｌｙＳｉ）

ｃ．数100ÅのグレインをもつＰｏｌｙＳｉ。

（Ａｓをドーピングしたポリシ（なおこのポリシは610℃で堆積し、600℃で15時間アニールしたものである））

ｄ．10Å以下のグレインをもつＰｏｌｙＳｉ（ＡｍｏｒｐｈｏｐｕｓＳｉ）

（ＰｏｌｙＳｉにSi^+イオン注入して測定）

第３図～第６図に各々示す曲線Ａ～Ｄは、それぞれ前記ａ～ｄの各測定用のサンプルについて、200nm～400nmの範囲内で測定を行い、反射率50～100%の間をプロットしたものである。

図示の如く、第３図（単結晶Ｓｉ）、第４図（数千ÅのグレインをもつＰｏｌｙＳｉ）のスペクトル曲線Ａ，Ｂは、235nm，330nm付近に極小があり、この間の270～280nmにピークが生ずる。第５図（数百ÅのグレインをもつＰｏｌｙＳｉ）のスペクトル曲線ｃは、330nm付近では極小をとらず、変曲点になっており、235nm付近の極小も、変曲点に近いものになっている。しかしその間の270～280nmには、ピークが見られる。一方、第６図のアモルファスＳｉのスペクトル曲線Ｄの場合、もはや上記極小、及びピークは見られない。

本実施例においては、これらのスペクトルについて240nm及び340nmの極小点（または変曲点）を直線で結び、そこに形成されるピークの面積を算出した。但し本実施例では、具体的には図示の如く２つの極小点（変曲点）付近に接するようにスペクトル曲線に接線を引いて、この接線とスペクトル曲線との囲む面積をもって、ピーク面積とした。つまり、ピーク面積を得るための直線を引く２点として、上記極小点（変曲点）付近の接点を用いたものである。

また本実施例においては、ピーク面積を算出の簡単なピーク高さによって近似することもできる。このピーク高さは、スペクトル曲線のピークから、２つの極小点（変曲点）付近に接する接線におろした垂線の高さを用いるものである。第３図乃至第５図に、このような垂線を符号Ｐａ～Ｐｃで示す。

さらに、測定精度は若干下るものの、スペクトル曲線のピークから垂直に引いた線の、２つの極小点（変曲点）付近に接する接線との交点までの長さによっても近似することもできる。

第７図のグラフⅠ～Ⅳは、前記の各サンプルごとのピーク面積とＴＥＭによって予め測定してあるグレインサイズとをプロットした結果を示す。ＴＥＭの測定ではグレインサイズの分布に幅があるので、グラフⅠ～Ⅳもサイズ方向に幅をもつようになっている。この結果から、検量線としてグラフⅤが得られ、これから前述の式が導かれる。従って、この式の導いたのと同じ条件で被測定体の反射紫外スペクトルを求め、上記ピーク面積を求めれば、この式によって結晶のグレインサイズを知ることができ、これにより被測定体のＳｉ結晶性を測定できる。

なおＴＥＭによる測定では、グレインサイズの分布に大小が現れてくるので、この式によって得られるグレインサイズは、平均的な値となっていると考えられる。また、２．０μｍ以上のグレインを有するＰｏｌｙＳｉのピーク面積と、単結晶Ｓｉのそれとの間には差異を見出すことができないため、本実施例の方法は20μｍ以下のグレインに関してのみ有効である。しかし、通常は数拾～数千ÅのPolySiがほとんどであるので、不都合はない。

なお、上述した如く、第７図のピーク面積の代わりにピーク高さ、あるいは垂線の長さを用いても同様に被測定

体のＳｉ結晶性を測定できる。
なお、この方法はＰｏｌｙＳｉの他にも、Si^+ をイオン注入した単結晶Ｓｉ表面等の表面結晶の解析の一部としても適用可能である。
また、Ｓｉの他にも、ＧｅやＡｓの反射スペクトルを測定しても、夫々、280nm，250nm付近にピークが見られ、Ｓｉと同様に結晶性を測定することができる。
さらに、この方法は上述のものに限らず、共有結合半導体であればこの紫外域でピークを持つので同様に測定できるものであり、上述したＧｅ，ＧａＡｓ，や、Ｃ，ＳｉＣ，あるいはそれらの多結晶体等の評価にも適用できる。

〔発明の効果〕

以上のように本発明の結晶性の測定方法は、簡単な操作で、短時間かつ低コストで、しかも非破壊の状態において、結晶性を測定できる。

＊従って本発明は、例えば半導体の製造工程などにおけるインプロセスでのインライン測定方法として具体化することも可能であるという効果がある。

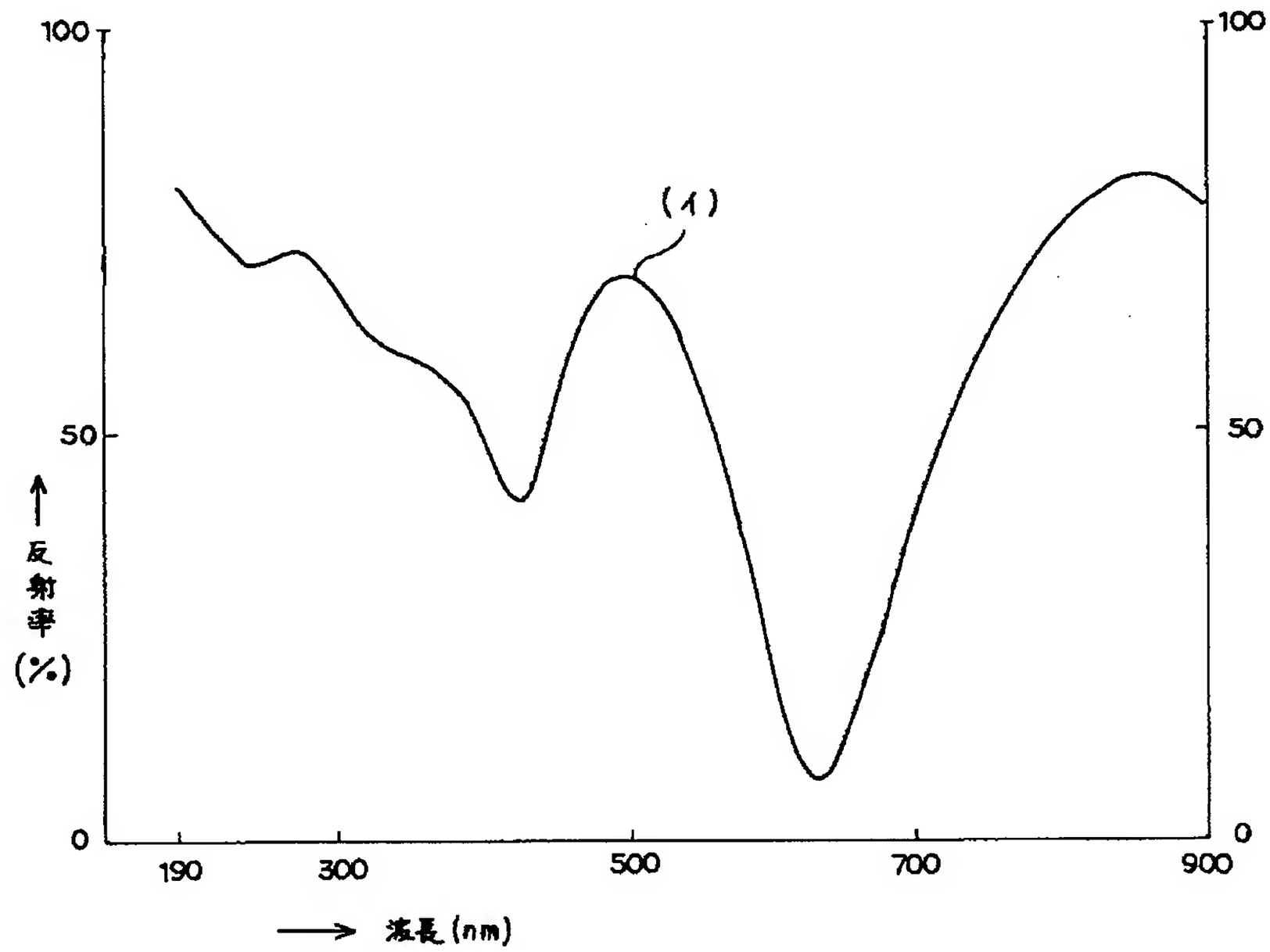
【図面の簡単な説明】

第１図は石英上ＰｏｌｙＳｉの反射スペクトルを示すグラフ、第２図は第１図のＰｏｌｙＳｉにSi^+ イオン注入、アニールを行ったサンプルの反射スペクトルを示すグラフ、第３図は単結晶Ｓｉの反射スペクトルを示すグラフ、第４図は数千ÅのグレインをもつＰｏｌｙＳｉの反射スペクトルを示すグラフ、第５図は数百ÅのグレインをもつＰｏｌｙＳｉの反射スペクトルを示すグラフ、第６図は10Å以下のグレインをもつＰｏｌｙＳｉの反射スペクトルを示すグラフ、第７図はグレインサイズとピーク面積との関係を示すグラフである。

（イ），（ロ），Ａ～Ｄ…スペクトル曲線。

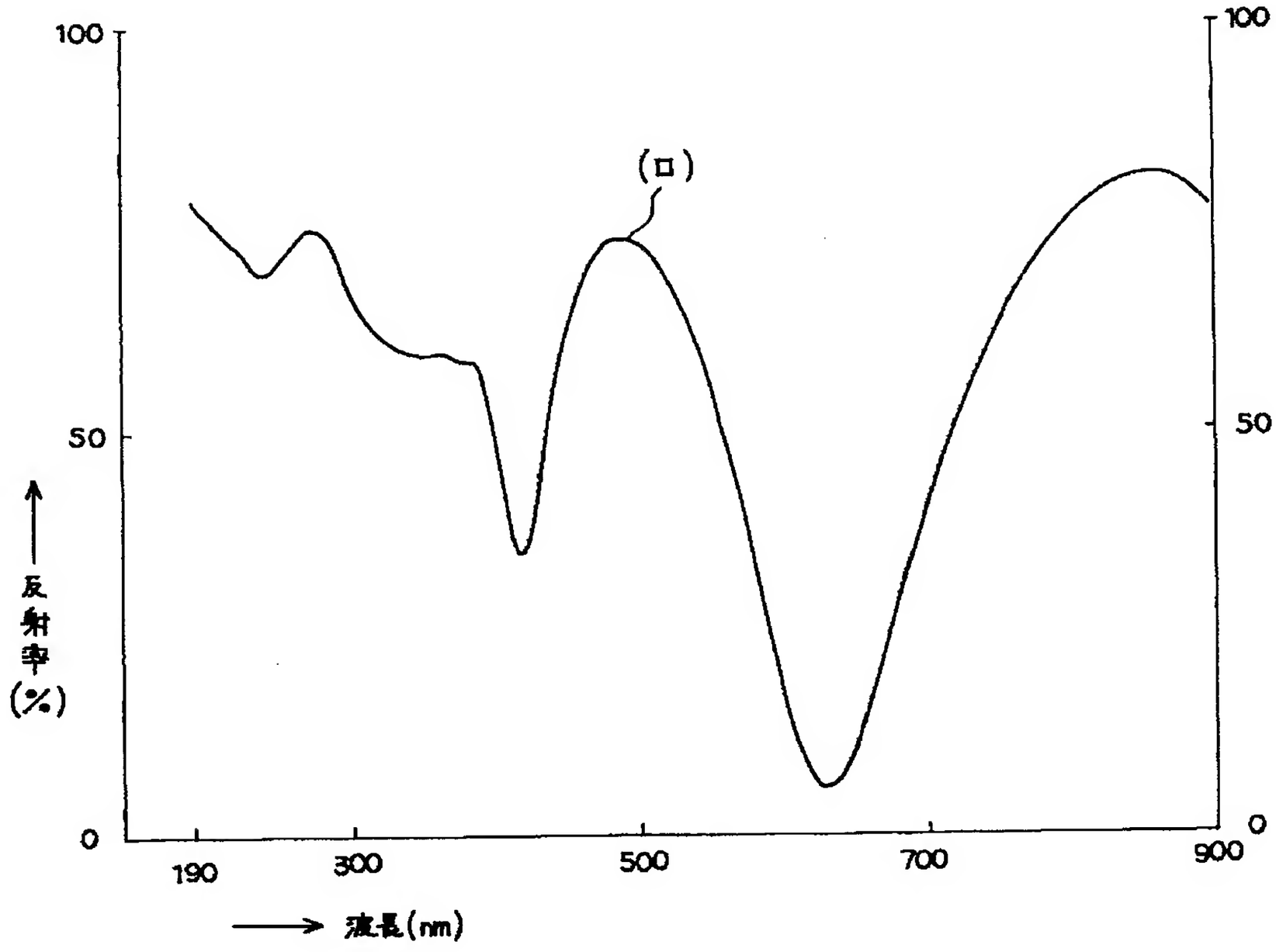
＊

【第１図】



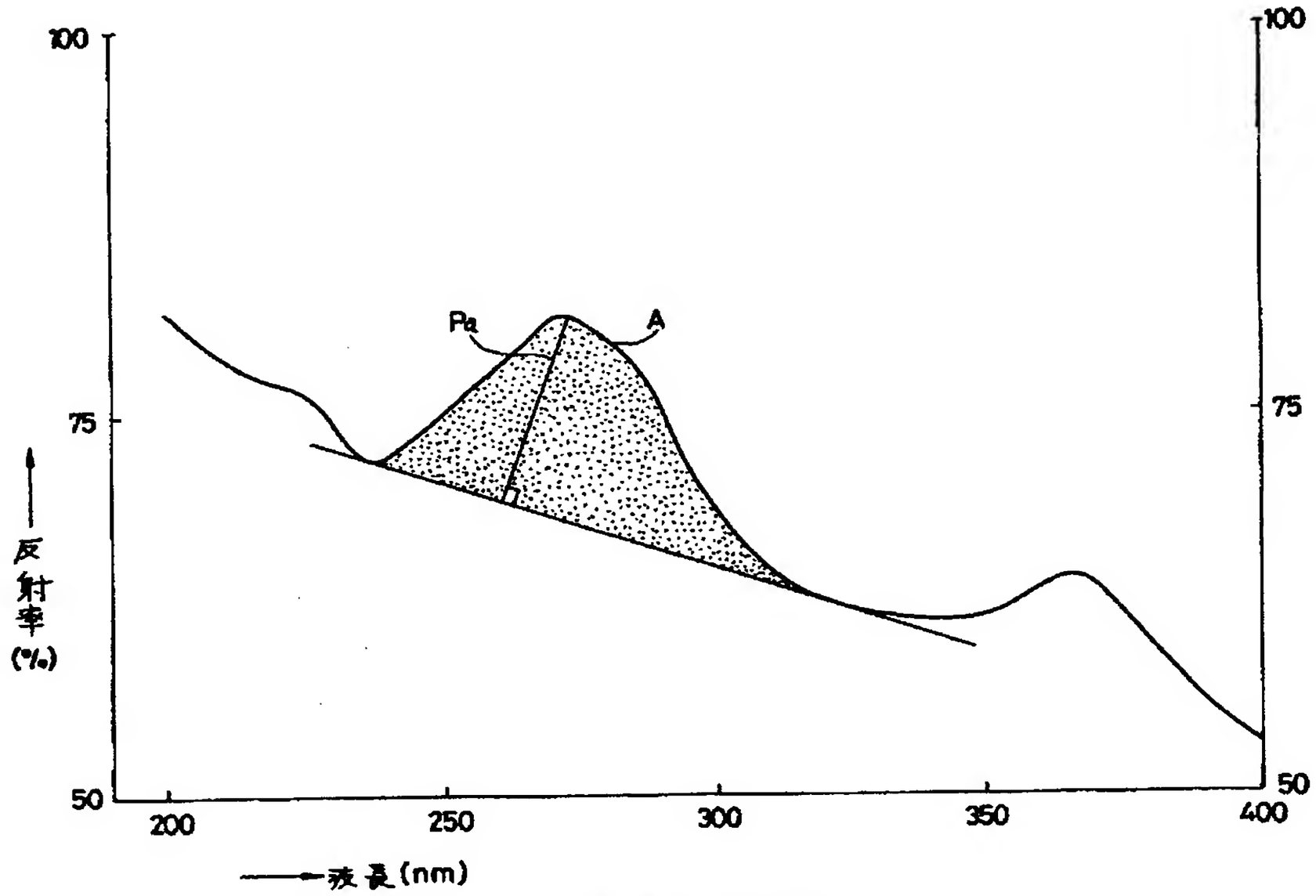
石英上 Poly Si (800Å) の反射スペクトル

【第２図】



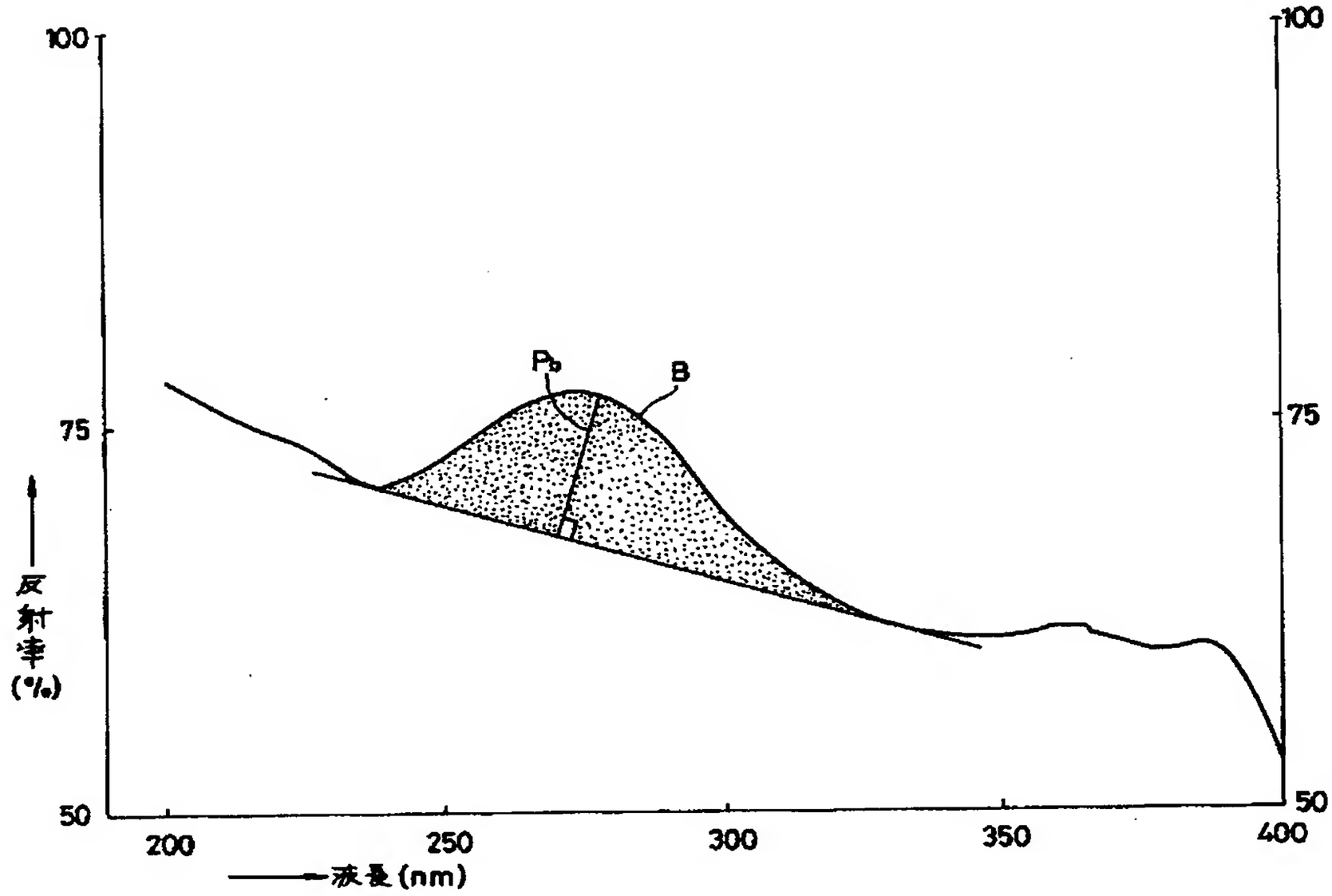
Si⁺イオン注入600℃アニール Poly Siの反射スペクトル

【第３図】



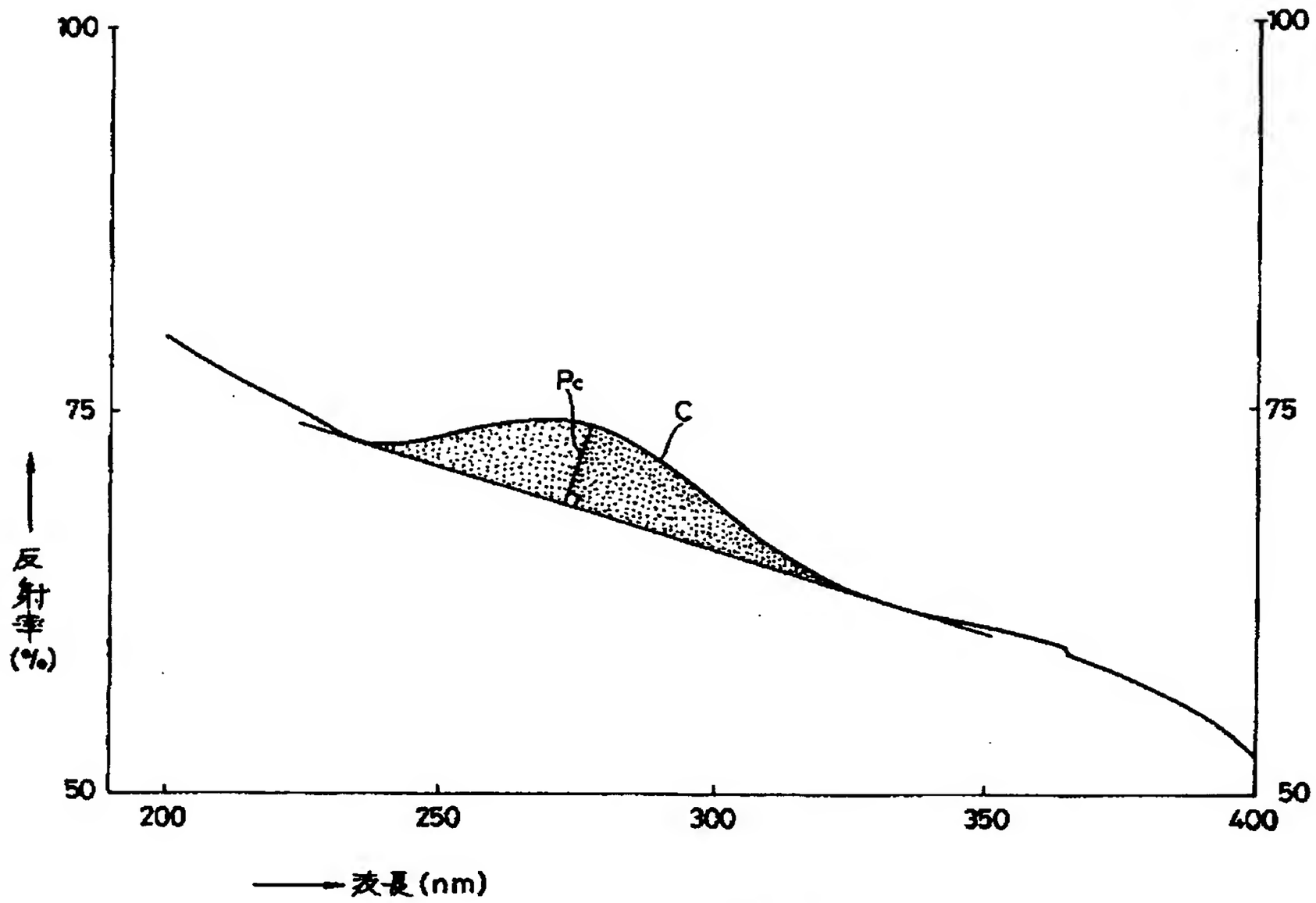
単結晶Siの場合

【第４図】



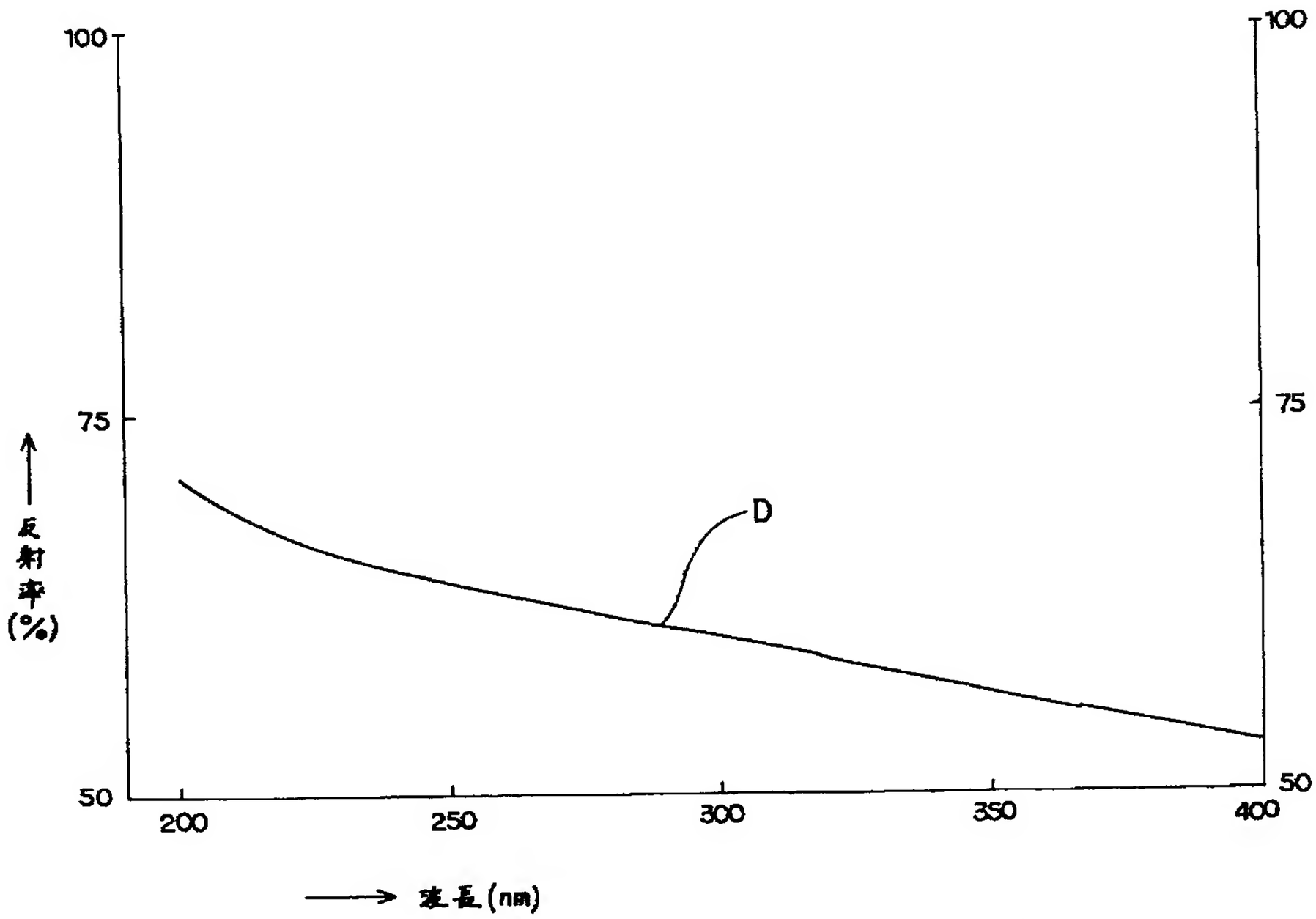
Si⁺イオン注入600°c 15hアニールしたPoly Siの場合

【第５図】



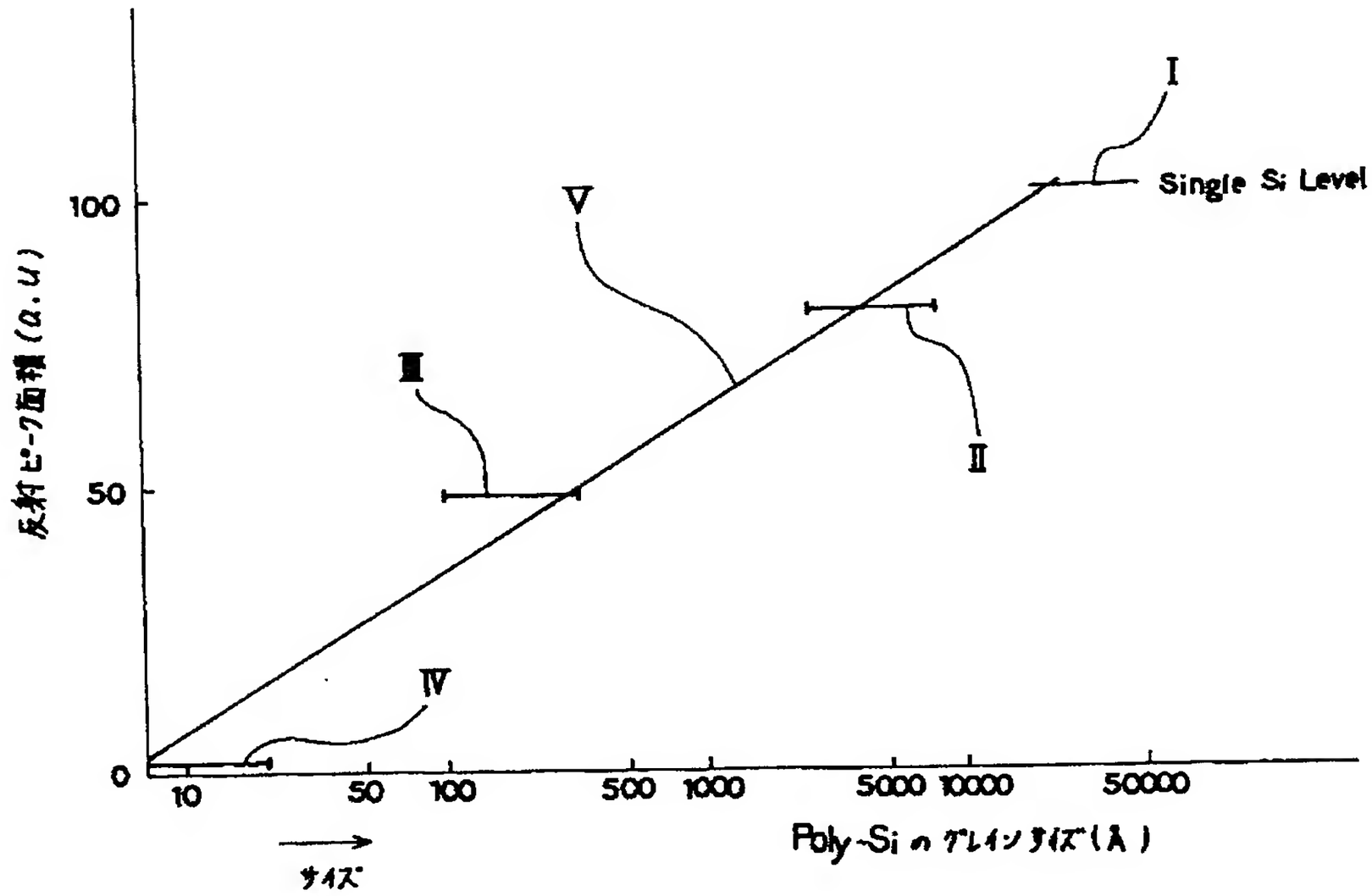
As depo poly Si の場合

【第６図】



Amorphous Si の場合 (poly Si に Si^+ イオン注入した直後)

【第７図】



グレインサイズと面積との関係

JP,06-007101,B

CLAIMS

[Claim(s)]

[Claim 1] The crystalline measuring method which measures the grain size of the crystal concerned from the area of the line which is the approach of measuring the crystallinity of a crystal using UV spectroscopy, asks for two pole dots or point of inflection depending on the grain size of the crystal in the surface reflectance spectrum curve of the measured body, and connects the point concerned or the line which connects the point near [concerned] the point, and the above-mentioned spectrum curve to surround.

[Claim 2] The crystalline measuring method which measures the grain size of the crystal concerned from the height of the perpendicular which took down to the line which is the approach of measuring the crystallinity of a crystal using UV spectroscopy, asks for two pole dots or the point of inflection depending on the grain size of the crystal in the surface reflectance spectrum curve of the measured body, and connects this point of this describing above from the maximum point of the above-mentioned spectrum curve between the points concerned, or the line which connects the point near [concerned] the point.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[Industrial Application]

This invention relates to the crystalline measuring method of covalent-bond semiconducting crystals, such as Si, germanium, C, SiC, and GaAs. In the industrial field treating for example, Si crystal, for example, the semi-conductor field, this invention can be used in order to measure the crystallinity of PolySi (polycrystalline silicon), and the crystallinity of Si substrate front face.

[Summary of the Invention]

This invention asks for two pole dots or point of inflection depending on the grain size of the

crystal in the surface reflectance spectrum curve of the measured body. The area of the line which connects the point concerned or the line which connects the point near [concerned] the point, and the above-mentioned spectrum curve to surround, Or by measuring the grain size of the crystal concerned from the height of the perpendicular taken down from the maximum point of the above-mentioned spectrum curve between the points concerned to the line which connects the point concerned, or the line which connects the point near [concerned] the point It is related with the crystalline measuring method with which long duration was conventionally required and measurement within a process moreover also enabled in-line measurement [in / for the difficult crystalline measurement / a semi-conductor process etc.] simple.

[Description of the Prior Art]

Conventionally, it was difficult to measure promptly simple the crystallinity, especially its crystal grain size about the crystal Si used in various fields. Especially the thing for which the grain size of a crystal is measured in this process in the production process which uses Crystal Si as ingredient is not performed.

For example, although PolySi was used in many fields in various electron devices, to have been possible for the monitor in the automatic production process of PolySi was not made into the object of an in process monitor until now, in spite of having been thickness, a refractive index, and dust extent, and the grain size's having been important on the property of the versatility of PolySi and having been an important factor when using especially PolySi as a resistor or a thin film transistor. This is because measurement of the grain size of PolySi was conventionally performed using TEM. That is, it is because it is necessary to measure the size of each grain using a transmission electron microscope in measurement by TEM so, and test portion production of thin-film-izing a sample takes long duration and cost moreover becomes high. although the crystallinity of Si substrate front face is an important factor on the property similarly and the measurement by the RBS approach is possible, when [moreover,] the measuring time becomes long as for the RBS approach -- surface **** -- it has the fault that the measurement in the thin range (for example, the range of 100A or less) is difficult.

[Problem(s) to be Solved by the Invention]

As mentioned above, each conventional measuring method is complicated, and requires a long time, therefore has the problem of being inapplicable to the monitor of the GURAIN size for example, in semi-conductor manufacture process in-line.

The object of this invention is to offer the crystalline measuring method which also made it possible to solve this problem, to be easy actuation, to be a short time and low cost, and to be able to measure that crystallinity simple by moreover getting to know the grain size of a crystal in the condition of not destroying, and to perform this measurement in an in process into [various] a process.

[Technical means which solve a problem]

The measuring method of Si crystallinity concerning this invention, for example Measure the crystallinity of Si crystal using UV spectroscopy, and it asks for two pole dots or point of inflection depending on the grain size of Si crystal in the surface reflectance spectrum curve of the measured body. The area of the line which connects the point concerned or the line which connects the point near [concerned] the point, and the above-mentioned spectrum curve to surround, Or the problem of the above-mentioned conventional technique is solved by taking the technical means which measure the grain size of the Si crystal concerned from the height of the perpendicular taken down from the maximum point of the above-mentioned spectrum curve between the points concerned to the line which connects the point concerned, or the line which connects the point near [concerned] the point.

In the surface reflectance spectrum curve of the measured body at the time of using UV spectroscopy, the spectrum configuration in 235nm and 330nm usually corresponds to the grain size of Si crystal. That is, a 270-280nm peak expresses the crystallinity of Si crystal, especially PolySi, and the minimum or point of inflection appears in 235nm and near 330nm these both sides. Therefore, the height of the perpendicular taken down from the maximum point of the area which the line which connects this two pole dots or point of inflection, and a spectrum curve surround, or the spectrum curve between two points to the line which connects two points serves as data corresponding to the peak showing the crystallinity of the above-mentioned Si crystal. Therefore, the grain size of Si crystal can be known using this, and, thereby, Si crystallinity can be measured. The height of the area which this tangent and the above-mentioned spectrum curve at the time of drawing a tangent so that the above-mentioned pole dot or point of inflection may not be connected directly, for example, it may touch near the pole dot concerned or the point of inflection surround, or the perpendicular taken down from the maximum point of the spectrum curve between two points to the tangent can also be used as a thing showing grain size. Thus, a contact can be used, and also you may find the height of the perpendicular taken down from the

maximum point of the spectrum curve between the points which connect the above-mentioned pole dot, point of inflection, and a point with relation, and have the area of it and a spectrum curve to surround, or its relation to it, and you may also consider as the data related to grain size similarly (such an area is called peak area below and the height of such a perpendicular is called peak height).

[Function of the Invention]

As mentioned above, according to the measuring method of this invention, the data which express grain size with the surface reflective ultraviolet spectroscopy spectrum of the measured body are obtained. If the surface reflectance spectrum of a proper is obtained in each grain size and the data of the above-mentioned area about each grain size or the above-mentioned height are investigated about what followed, for example, measured grain size to accuracy beforehand by TEM, the grain size of the crystal of the measured body can be known by carrying out the comparison response of this and the data obtained by the above-mentioned location survey. Since what is necessary is just according to this measuring method to measure the surface reflectance spectrum of the measured body although required data are obtained, moreover, measurement can be done simple for a short time, and, moreover, the measured body can be measured by un-destroying. For this reason, this invention can be used also as an in-line crystalline measuring method, and can also be applied as an in process monitor.

[Example]

Hereafter, one example of this invention is described. However, although it is natural, this invention is not limited only to the example described below.

This example applies this invention to the approach of measuring the grain size of PolySi using an ultraviolet reflectance spectrum. Specifically, the surface reflectance spectrum was measured using the spectrophotometer of the light.

According to the approach of this example, since relation like a degree type is realized between grain size (R) and a reflective peak area (A), grain size can be measured using this. This formula is obtained [size / its / each / the grain size measured beforehand and / grain] by TEM based on the data about the reflective peak area of the proper measured beforehand about the sample of some [the conditions described below].

A=27xlog(R)-20 (however, peak area when A sets single crystal silicon to 100)

Hereafter, progress of an experiment is shown [which came to draw this formula].

Drawing 1 shows typical reflectance spectrum curvilinear (b) of PolySi deposited and formed on the quartz. The thickness of this PolySi is 800A and deposition temperature is 610 degrees C. In addition, at the time of reflectance spectrum measurement, the scan speed was made into medium speed and the slit was measured as 2.0nm (it is below the same).

Drawing 2 is graph (b) which shows the reflectance spectrum in the case of the sample which carried out the ion implantation of Si+ to PolySi of drawing 1 on condition that 40keV(s) and 1x1015cm-2, and it annealed for 15 hours and was obtained at 600 degrees C. The peak which appears in the range of 270-280nm in this is a peak wave showing the crystallinity of PolySi. In addition, the spectrum 400nm or more expresses the interference property between PolySi and a quartz, and this is a wave showing relation with thickness. By the comparison with drawing 1 and drawing 2 , the direction of the sample of drawing 2 which performed Si+ ion implantation and annealing becomes what has a high peak so that clearly. Thus, area in case a spectrum is a peak was computed, and the correlation was investigated between the grain sizes of PolySi beforehand measured by TEM.

First, four kinds of things as follows were used as a sample for measurement.

a. Single crystal Si.

b. PolySi with a thousands of A grain.

(PolySi which carried out the ion implantation of Si+ and annealed at 600 degrees C for 15 hours)

c. PolySi with several 100A grain.

(PolySi which doped As (in addition, this PolySi is deposited at 610 degrees C, and is annealed at 600 degrees C for 15 hours))

d. PolySi with the grain of 10 or less A (AmorphopusSi)

(Si+ ion implantation is carried out to PolySi, and it measures)

About the sample for each measurement of said a-d, curvilinear A-D respectively shown in Figs. 3 - 6 measures within the limits of 200nm - 400nm, and plots between 50 - 100% of reflection factors, respectively.

Like a graphic display, the spectrum curves A and B of drawing 3 (single crystal Si) and drawing 4 (PolySi with a thousands of A grain) have the minimum 235nm and near 330nm, and a peak produces them in 270-280nm during this period. Near 330nm, the spectrum curve c of drawing 5 (PolySi with a hundreds of A grain) does not take the minimum, but has become point of

inflection, and has become what also has the minimum close to point of inflection near 235nm. However, a peak is looked at by 270-280nm of the meantime. On the other hand, in the case of the spectrum curve D of the amorphous silicon of drawing 6 , the above-mentioned minimum and a peak are not seen any longer.

In this example, the area of the peak formed in an epilogue and there in a straight line about these spectrums in a pole dot (240nm and 340nm) (or point of inflection) was computed. However, in this example, the tangent was drawn on the spectrum curve so that it might specifically touch near [two] a pole dot (point of inflection) like a graphic display, and it had the area of this tangent and a spectrum curve to surround, and considered as the peak area. That is, the contact near [above-mentioned] a pole dot (point of inflection) is used as two points which draw the straight line for obtaining a peak area.

Moreover, in this example, a peak area can also be approximated with the easy peak height of calculation. The height of the perpendicular taken down from the peak of a spectrum curve to the tangent which touches near [two] a pole dot (point of inflection) is used for this peak height. Such a perpendicular is shown in Figs. 3 thru/or 5 by sign Pa-Pc.

Furthermore, although the accuracy of measurement is gone down a little, it can also approximate also with the die length by the intersection with the tangent which touches near [two] the pole dot (point of inflection) of the line vertically drawn from the peak of a spectrum curve.

Graph I-IV of drawing 7 shows the result of having plotted the peak area for every aforementioned sample, and the grain size beforehand measured by TEM. Since width of face is in distribution of grain size in measurement of TEM, graph I-IV also has width of face in the size direction. From this result, Graph V is obtained as a calibration curve and the formula of the future above-mentioned is drawn. Therefore, if it asks for the reflective ultraviolet spectrum of the measured body on the same conditions as this formula led and asks for the above-mentioned peak area, by this formula, the grain size of a crystal can be known and, thereby, the Si crystallinity of the measured body can be measured. In addition, by measurement by TEM, since size appears in distribution of grain size, it is thought that the grain size obtained by this formula serves as an average value. Moreover, since a difference cannot be found out between the peak area of PolySi which has a grain 2.0 micrometers or more, and it of a single crystal Si, the approach of this example is effective only about a grain 20 micrometers or less. However, since

PolySi of several 10 - 1000A of numbers is usually most, there is no inconvenience. In addition, as mentioned above, even if it uses a peak height or the die length of a perpendicular instead of the peak area of drawing 7 , the Si crystallinity of the measured body can be measured similarly. In addition, this approach is applicable also as a part of analysis of surface crystals, such as a single crystal Si front face which carried out the ion implantation of Si+ other than PolySi. Moreover, even if it measures germanium and the reflectance spectrum of As other than Si, a peak is seen 280nm and near 250nm, and crystallinity can be measured like Si, respectively. Furthermore, this approach is applicable also to assessment of not only an above-mentioned thing but the germanium and GaAs which can measure similarly since it has a peak by this ultraviolet area if it is a covalent-bond semi-conductor, and were mentioned above, **, C and SiC(s), or those polycrystalline substance etc.

[Effect of the Invention]

As mentioned above, the crystalline measuring method of this invention is easy actuation, are a short time and low cost, and, moreover, can measure crystallinity in the condition of not destroying.

Therefore, this invention is effective also in it being possible to take shape as an in-line measuring method in the in process in the production process of a semi-conductor etc.

TECHNICAL FIELD

[Industrial Application]

This invention relates to the crystalline measuring method of covalent-bond semiconducting crystals, such as Si, germanium, C, SiC, and GaAs. In the industrial field treating for example, Si crystal, for example, the semi-conductor field, this invention can be used in order to measure the crystallinity of PolySi (polycrystalline silicon), and the crystallinity of Si substrate front face.

[Summary of the Invention]

This invention asks for two pole dots or point of inflection depending on the grain size of the crystal in the surface reflectance spectrum curve of the measured body. The area of the line which connects the point concerned or the line which connects the point near [concerned] the point, and the above-mentioned spectrum curve to surround, Or by measuring the grain size of the crystal concerned from the height of the perpendicular taken down from the maximum point of the above-mentioned spectrum curve between the points concerned to the line which connects the point concerned, or the line which connects the point near [concerned] the point It is related

with the crystalline measuring method with which long duration was conventionally required and measurement within a process moreover also enabled in-line measurement [in / for the difficult crystalline measurement / a semi-conductor process etc.] simple.

PRIOR ART

[Description of the Prior Art]
Conventionally, it was difficult to measure promptly simple the crystallinity, especially its crystal grain size about the crystal Si used in various fields. Especially the thing for which the grain size of a crystal is measured in this process in the production process which uses Crystal Si as ingredient is not performed.
For example, although PolySi was used in many fields in various electron devices, to have been possible for the monitor in the automatic production process of PolySi was not made into the object of an in process monitor until now, in spite of having been thickness, a refractive index, and dust extent, and the grain size's having been important on the property of the versatility of PolySi and having been an important factor when using especially PolySi as a resistor or a thin film transistor. This is because measurement of the grain size of PolySi was conventionally performed using TEM. That is, it is because it is necessary to measure the size of each grain using a transmission electron microscope in measurement by TEM so, and test portion production of thin-film-izing a sample takes long duration and cost moreover becomes high. although the crystallinity of Si substrate front face is an important factor on the property similarly and the measurement by the RBS approach is possible, when [moreover,] the measuring time becomes long as for the RBS approach -- surface **** -- it has the fault that the measurement in the thin range (for example, the range of 100A or less) is difficult.
EFFECT OF THE INVENTION

[Effect of the Invention]

As mentioned above, the crystalline measuring method of this invention is easy actuation, are a short time and low cost, and, moreover, can measure crystallinity in the condition of not destroying.

Therefore, this invention is effective also in it being possible to take shape as an in-line measuring method in the in process in the production process of a semi-conductor etc.

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention]
As mentioned above, each conventional measuring method is complicated, and requires a long time, therefore has the problem of being inapplicable to the monitor of the GURAIN size for example, in semi-conductor manufacture process in-line.
The object of this invention is to offer the crystalline measuring method which also made it possible to solve this problem, to be easy actuation, to be a short time and low cost, and to be

able to measure that crystallinity simple by moreover getting to know the grain size of a crystal in the condition of not destroying, and to perform this measurement in an in process into [various] a process.

MEANS

[Technical means which solve a problem]

The measuring method of Si crystallinity concerning this invention, for example Measure the crystallinity of Si crystal using UV spectroscopy, and it asks for two pole dots or point of inflection depending on the grain size of Si crystal in the surface reflectance spectrum curve of the measured body. The area of the line which connects the point concerned or the line which connects the point near [concerned] the point, and the above-mentioned spectrum curve to surround, Or the problem of the above-mentioned conventional technique is solved by taking the technical means which measure the grain size of the Si crystal concerned from the height of the perpendicular taken down from the maximum point of the above-mentioned spectrum curve between the points concerned to the line which connects the point concerned, or the line which connects the point near [concerned] the point.

In the surface reflectance spectrum curve of the measured body at the time of using UV spectroscopy, the spectrum configuration in 235nm and 330nm usually corresponds to the grain size of Si crystal. That is, a 270-280nm peak expresses the crystallinity of Si crystal, especially PolySi, and the minimum or point of inflection appears in 235nm and near 330nm these both sides. Therefore, the height of the perpendicular taken down from the maximum point of the area which the line which connects this two pole dots or point of inflection, and a spectrum curve surround, or the spectrum curve between two points to the line which connects two points serves as data corresponding to the peak showing the crystallinity of the above-mentioned Si crystal. Therefore, the grain size of Si crystal can be known using this, and, thereby, Si crystallinity can be measured. The height of the area which this tangent and the above-mentioned spectrum curve at the time of drawing a tangent so that the above-mentioned pole dot or point of inflection may not be connected directly, for example, it may touch near the pole dot concerned or the point of inflection surround, or the perpendicular taken down from the maximum point of the spectrum curve between two points to the tangent can also be used as a thing showing grain size. Thus, a contact can be used, and also you may find the height of the perpendicular taken down from the maximum point of the spectrum curve between the points which connect the above-mentioned

pole dot, point of inflection, and a point with relation, and have the area of it and a spectrum curve to surround, or its relation to it, and you may also consider as the data related to grain size similarly (such an area is called peak area below and the height of such a perpendicular is called peak height).

OPERATION

[Function of the Invention]

As mentioned above, according to the measuring method of this invention, the data which express grain size with the surface reflective ultraviolet spectroscopy spectrum of the measured body are obtained. If the surface reflectance spectrum of a proper is obtained in each grain size and the data of the above-mentioned area about each grain size or the above-mentioned height are investigated about what followed, for example, measured grain size to accuracy beforehand by TEM, the grain size of the crystal of the measured body can be known by carrying out the comparison response of this and the data obtained by the above-mentioned location survey. Since what is necessary is just according to this measuring method to measure the surface reflectance spectrum of the measured body although required data are obtained, moreover, measurement can be done simple for a short time, and, moreover, the measured body can be measured by un-destroying. For this reason, this invention can be used also as an in-line crystalline measuring method, and can also be applied as an in process monitor.

EXAMPLE

[Example]

Hereafter, one example of this invention is described. However, although it is natural, this invention is not limited only to the example described below.

This example applies this invention to the approach of measuring the grain size of PolySi using an ultraviolet reflectance spectrum. Specifically, the surface reflectance spectrum was measured using the spectrophotometer of the light.

According to the approach of this example, since relation like a degree type is realized between grain size (R) and a reflective peak area (A), grain size can be measured using this. This formula is obtained [size / its / each / the grain size measured beforehand and / grain] by TEM based on the data about the reflective peak area of the proper measured beforehand about the sample of some [the conditions described below].

A=27xlog(R)-20 (however, peak area when A sets single crystal silicon to 100)

Hereafter, progress of an experiment is shown [which came to draw this formula].

Drawing 1 shows typical reflectance spectrum curvilinear (b) of PolySi deposited and formed on the quartz. The thickness of this PolySi is 800A and deposition temperature is 610 degrees C. In addition, at the time of reflectance spectrum measurement, the scan speed was made into medium speed and the slit was measured as 2.0nm (it is below the same).

Drawing 2 is graph (b) which shows the reflectance spectrum in the case of the sample which carried out the ion implantation of Si+ to PolySi of drawing 1 on condition that 40keV(s) and 1x1015cm-2, and it annealed for 15 hours and was obtained at 600 degrees C. The peak which appears in the range of 270-280nm in this is a peak wave showing the crystallinity of PolySi. In addition, the spectrum 400nm or more expresses the interference property between PolySi and a quartz, and this is a wave showing relation with thickness. By the comparison with drawing 1 and drawing 2 , the direction of the sample of drawing 2 which performed Si+ ion implantation and annealing becomes what has a high peak so that clearly. Thus, area in case a spectrum is a peak was computed, and the correlation was investigated between the grain sizes of PolySi beforehand measured by TEM.

First, four kinds of things as follows were used as a sample for measurement.

a. Single crystal Si.

b. PolySi with a thousands of A grain.

(PolySi which carried out the ion implantation of Si+ and annealed at 600 degrees C for 15 hours)

c. PolySi with several 100A grain.

(PolySi which doped As (in addition, this PolySi is deposited at 610 degrees C, and is annealed at 600 degrees C for 15 hours))

d. PolySi with the grain of 10 or less A (AmorphopusSi)

(Si+ ion implantation is carried out to PolySi, and it measures)

About the sample for each measurement of said a-d, curvilinear A-D respectively shown in Figs. 3 - 6 measures within the limits of 200nm - 400nm, and plots between 50 - 100% of reflection factors, respectively.

Like a graphic display, the spectrum curves A and B of drawing 3 (single crystal Si) and drawing 4 (PolySi with a thousands of A grain) have the minimum 235nm and near 330nm, and a peak

produces them in 270-280nm during this period. Near 330nm, the spectrum curve c of drawing 5 (PolySi with a hundreds of A grain) does not take the minimum, but has become point of inflection, and has become what also has the minimum close to point of inflection near 235nm. However, a peak is looked at by 270-280nm of the meantime. On the other hand, in the case of the spectrum curve D of the amorphous silicon of drawing 6 , the above-mentioned minimum and a peak are not seen any longer.

In this example, the area of the peak formed in an epilogue and there in a straight line about these spectrums in a pole dot (240nm and 340nm) (or point of inflection) was computed. However, in this example, the tangent was drawn on the spectrum curve so that it might specifically touch near [two] a pole dot (point of inflection) like a graphic display, and it had the area of this tangent and a spectrum curve to surround, and considered as the peak area. That is, the contact near [above-mentioned] a pole dot (point of inflection) is used as two points which draw the straight line for obtaining a peak area.

Moreover, in this example, a peak area can also be approximated with the easy peak height of calculation. The height of the perpendicular taken down from the peak of a spectrum curve to the tangent which touches near [two] a pole dot (point of inflection) is used for this peak height. Such a perpendicular is shown in Figs. 3 thru/or 5 by sign Pa-Pc.

Furthermore, although the accuracy of measurement is gone down a little, it can also approximate also with the die length by the intersection with the tangent which touches near [two] the pole dot (point of inflection) of the line vertically drawn from the peak of a spectrum curve.

Graph I-IV of drawing 7 shows the result of having plotted the peak area for every aforementioned sample, and the grain size beforehand measured by TEM. Since width of face is in distribution of grain size in measurement of TEM, graph I-IV also has width of face in the size direction. From this result, Graph V is obtained as a calibration curve and the formula of the future above-mentioned is drawn. Therefore, if it asks for the reflective ultraviolet spectrum of the measured body on the same conditions as this formula led and asks for the above-mentioned peak area, by this formula, the grain size of a crystal can be known and, thereby, the Si crystallinity of the measured body can be measured. In addition, by measurement by TEM, since size appears in distribution of grain size, it is thought that the grain size obtained by this formula serves as an average value. Moreover, since a difference cannot be found out between the peak

area of PolySi which has a grain 2.0 micrometers or more, and it of a single crystal Si, the approach of this example is effective only about a grain 20 micrometers or less. However, since PolySi of several 10 - 1000A of numbers is usually most, there is no inconvenience. In addition, as mentioned above, even if it uses a peak height or the die length of a perpendicular instead of the peak area of drawing 7 , the Si crystallinity of the measured body can be measured similarly. In addition, this approach is applicable also as a part of analysis of surface crystals, such as a single crystal Si front face which carried out the ion implantation of Si+ other than PolySi. Moreover, even if it measures germanium and the reflectance spectrum of As other than Si, a peak is seen 280nm and near 250nm, and crystallinity can be measured like Si, respectively. Furthermore, this approach is applicable also to assessment of not only an above-mentioned thing but the germanium and GaAs which can measure similarly since it has a peak by this ultraviolet area if it is a covalent-bond semi-conductor, and were mentioned above, **, C and SiC(s), or those polycrystalline substance etc.

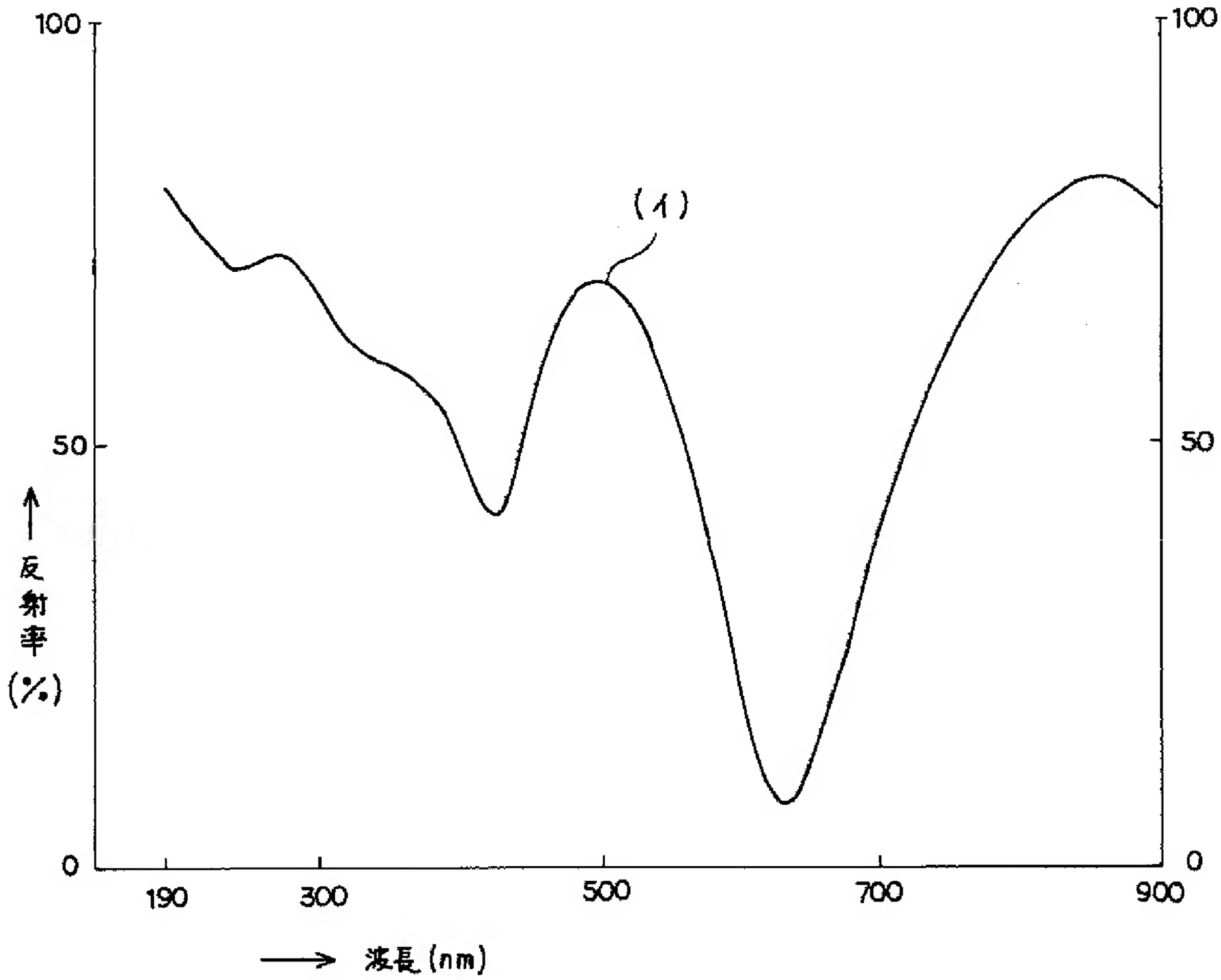
DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

The graph with which drawing 1 shows the reflectance spectrum on [PolySi] a quartz, and drawing 2 to PolySi of drawing 1 Si+ ion implantation, The graph which shows the reflectance spectrum of the sample which performed annealing, the graph with which drawing 3 shows the reflectance spectrum of a single crystal Si, The graph which shows the reflectance spectrum of PolySi in which drawing 4 has a thousands of A grain, The graph which shows the reflectance spectrum of PolySi in which drawing 5 has a hundreds of A grain, the graph which shows the reflectance spectrum of PolySi in which drawing 6 has a grain 10A or less, and drawing 7 are graphs which show the relation between grain size and a peak area.

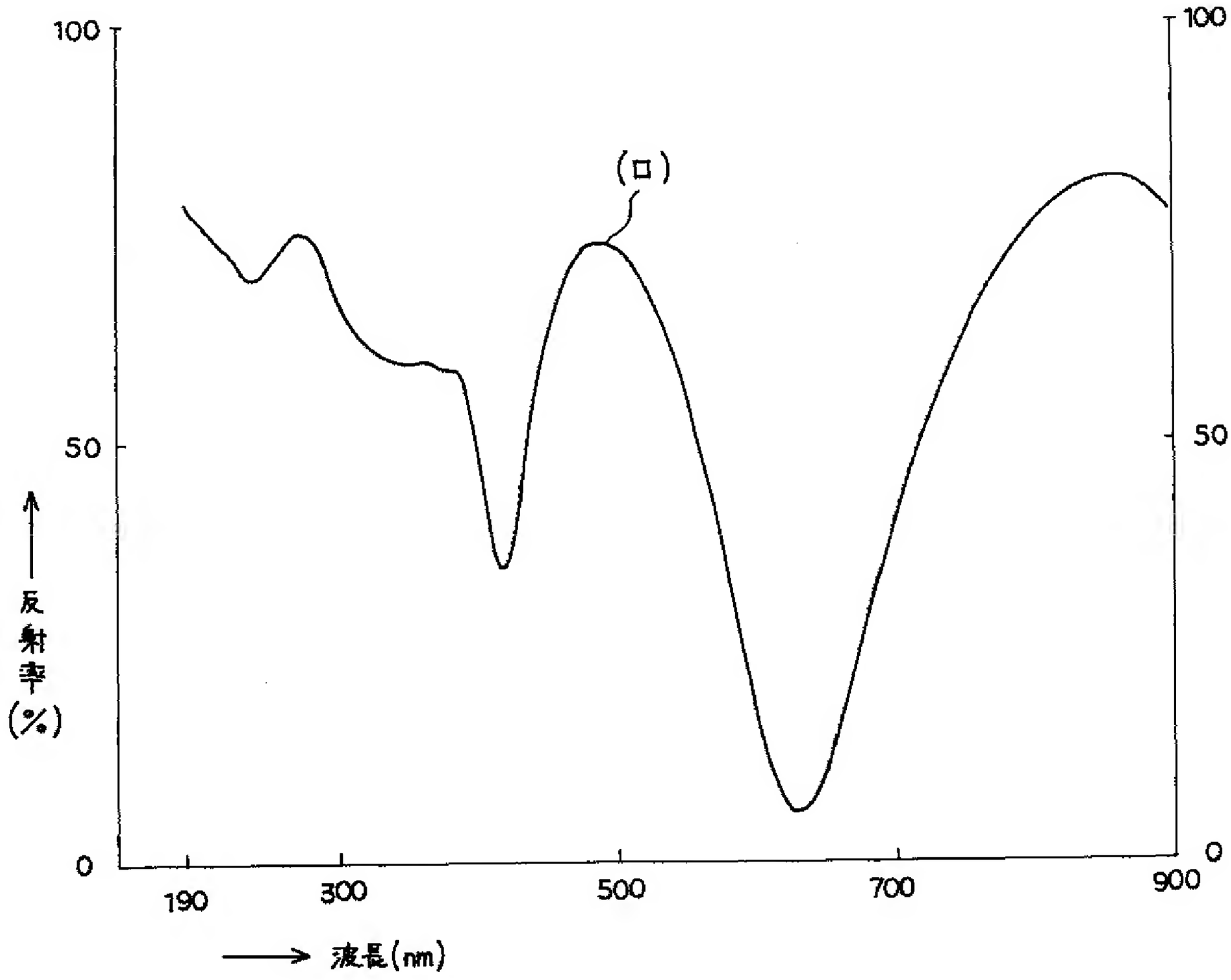
(b), (b), A-D -- Spectrum curve.

Drawing 1



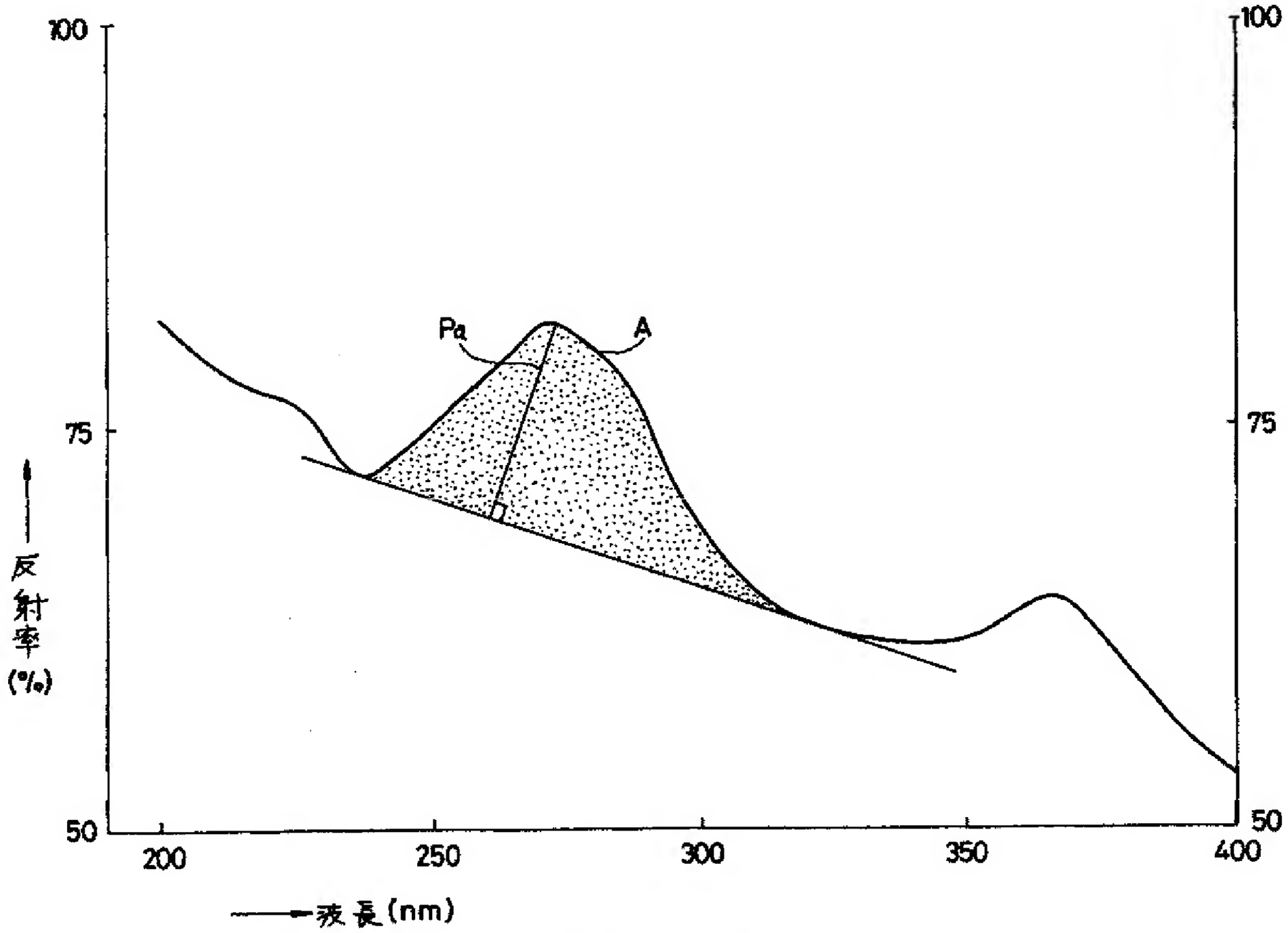
石英上 Poly Si (800 Å) の反射スペクトル

Drawing 2



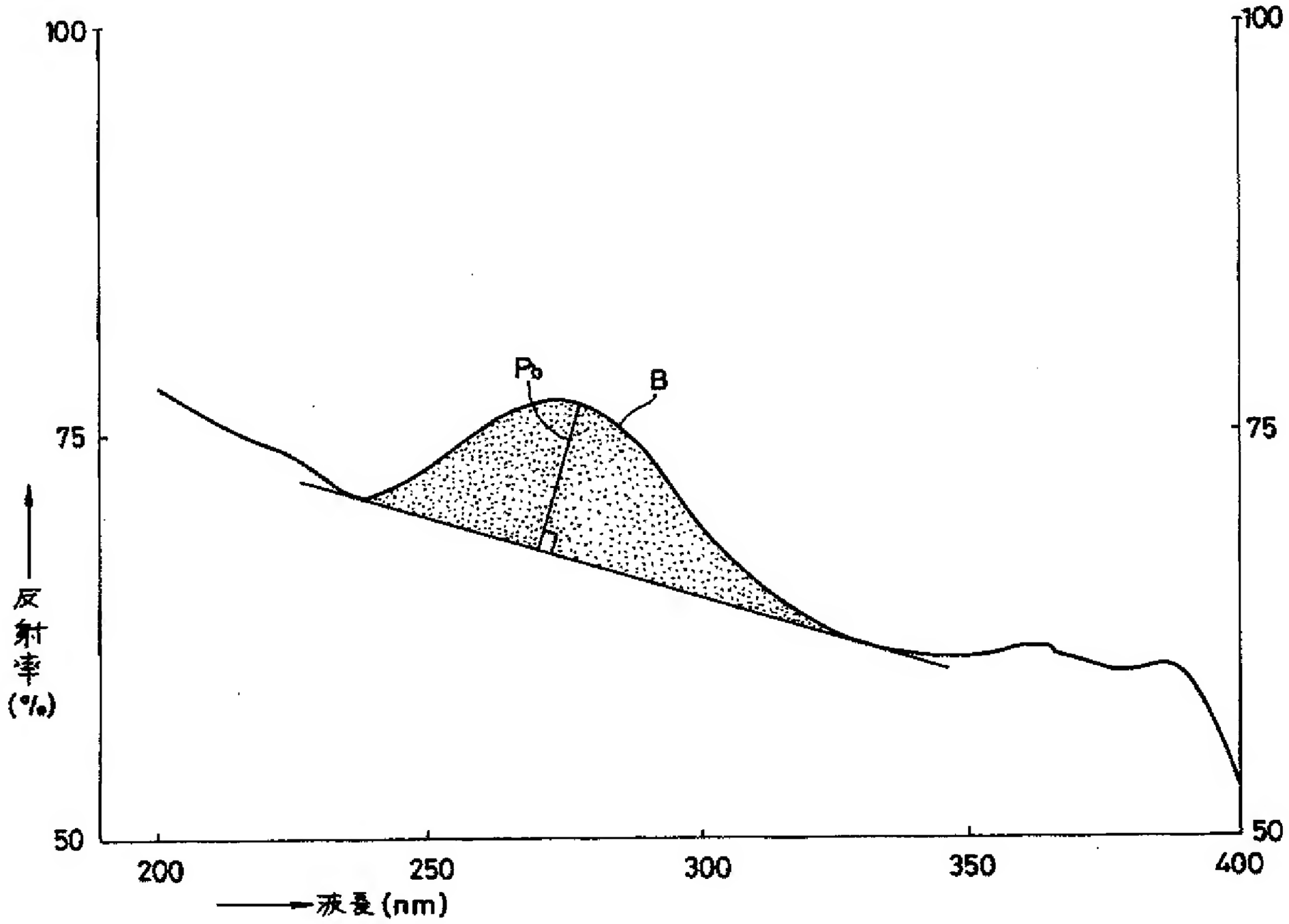
Si⁺イオン注入600℃アニール Poly Siの反射スペクトル

Drawing 3



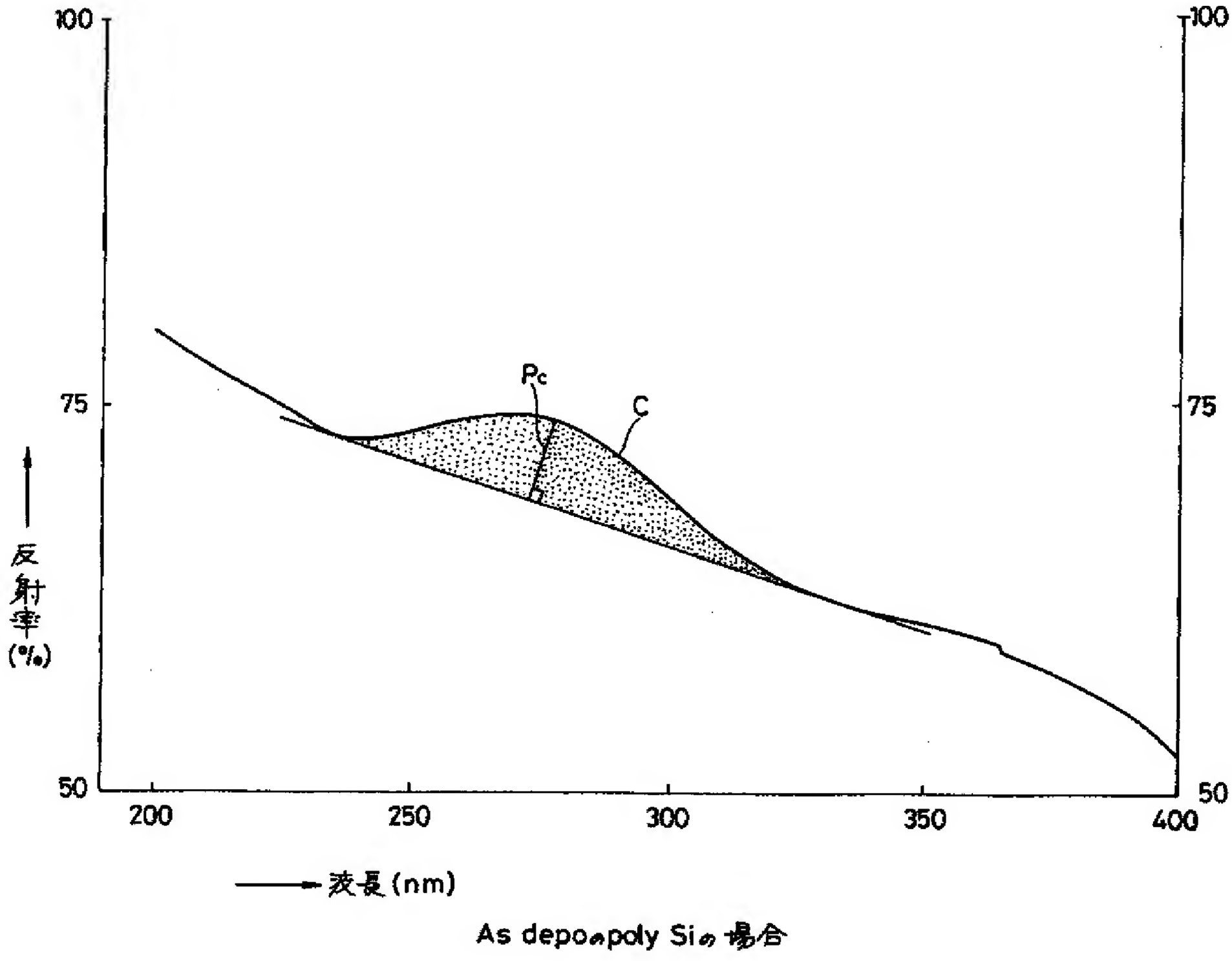
単結晶Siの場合

Drawing 4



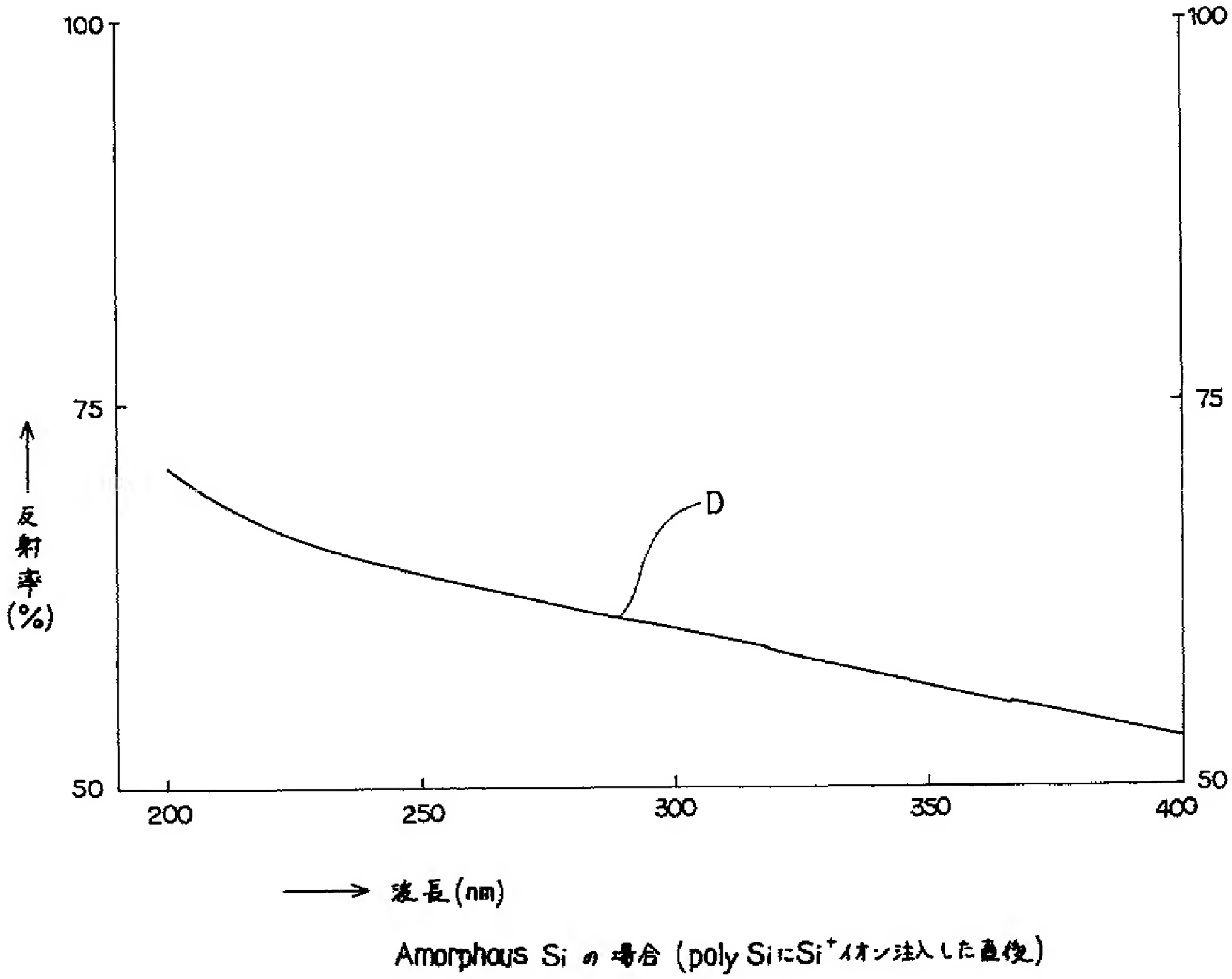
Si⁺イオン注入600°c 15hアニールしたPoly Siの場合

Drawing 5

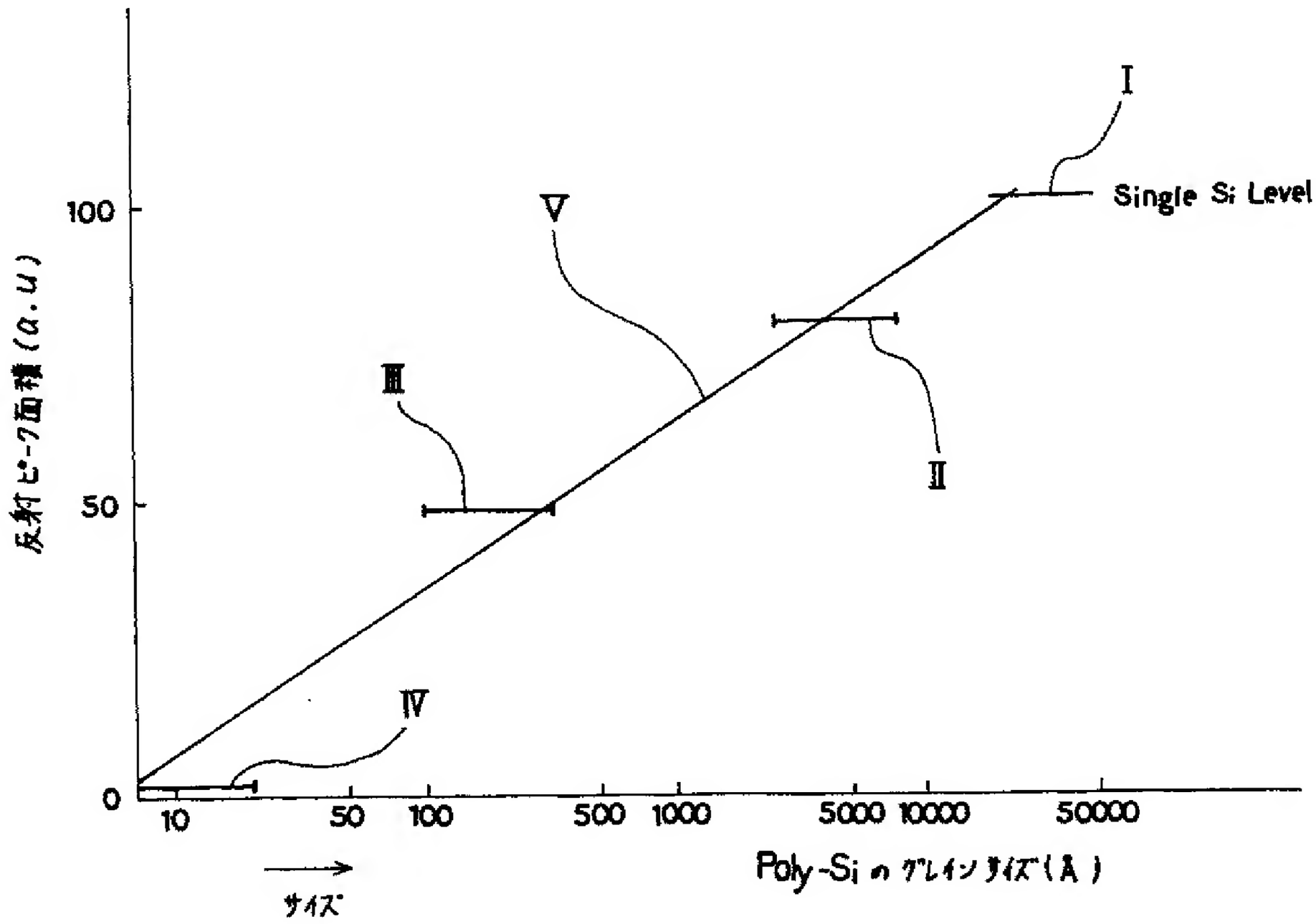


As depoのpoly Siの場合

Drawing 6


100
75
50
200
250
300
350
400
反射率(%)
D
波長(nm)
Amorphous Si の場合 (poly Si に Si⁺ イオン注入した直後)

Drawing 7



グレインサイズと面積との関係

PATENT ABSTRACTS OF JAPAN

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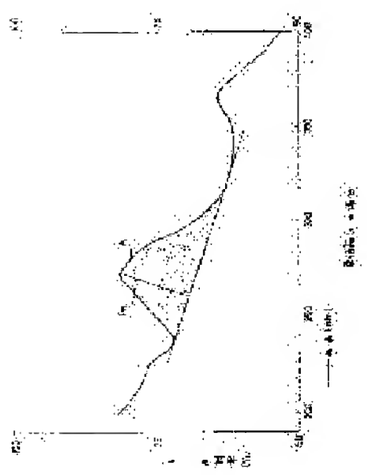
HOSHI TAEKO
NOGUCHI TAKASHI

(54) MEASURING METHOD FOR SI CRYSTALLINE PROPERTY



(57)Abstract:

PURPOSE: To measure the grain size of crystal on the surface of a sample from the area determined by a line connecting two minimal points, inflection points, or nearby points depending upon the crystal grain size on the surface reflection spectrum curve of the sample and the spectrum curve, or the height of a perpendicular from a maximal point between them.

CONSTITUTION: The surface reflection spectrum curve of Si single crystal when an ultraviolet spectral method is used corresponds to the size of a crystal grain normally between 235 and 330nm and indicates the crystal of poly-Si at a peak of 270W280nm and a minimal or inflection point appears almost between 235 and 330nm on both sides of the peak. The area surrounded with the line connecting said two points and spectrum curve

or height of the perpendicular from the maximal point of the curve is information corresponding to the peak where the crystalline property of the Si crystal is obtained, and this is used to measure the size and crystalline property of a crystal grain. Further, a tangent drawn nearby the minimal point and inflection point can be utilized. The information is compared with prepared information to judge the size of the crystal grain.

LEGAL STATUS

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